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Ultracapacitors as Energy and Power Storage Devices for Commercial and Military Applications

Ultracapacitors as Energy and Power Storage Devices for Commercial and Military Applications

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Ultracapacitors as Energy and Power Storage Devices for Commercial and Military Applications

Summary

Ultracapacitors (ultracaps) are energy storage devices capable of extremely rapid charge and discharge rates with the ability to be cycled hundreds of thousands of times. These unique capabilities make ultracaps attractive for a number of applications. The advantages over lithium ion batteries are somewhat mitigated by the fact that they have less than 10% of the specific energy (Wh/kg) and require a power converter to regulate their voltage. The high capacitance is achieved by the enormously high surface area of the carbon electrodes compared to planar electrolytic capacitors. Ultracapacitors are commonly used to provide voltage stabilization of power converters and to supplement peak-power loading of electrical systems. Their application has expanded from electronics and telecommunications to industrial load leveling and transportation. Due to their durability, their use in aerospace has been for munitions fusing and missile power load leveling. Ultimately, application will be pulsed power storage and delivery for electric propulsion and directed-energy weapons.

Recent developments in ultracapacitors have focused on different active materials and electrode designs. By using advanced carbons, polymers, and metal oxides, increased power density and energy density can be achieved. Oxide-based thin-film ultracaps have demonstrated high-performance energy and power density, approaching theoretical limits. Carbon nanotubes and advanced carbons have been used as additives to and solely as electrode materials. Nanostructured materials and thin-film manufacturing process improvements will generate breakthroughs in mass production. Magnetic capacitors are a recent development, manufactured using semiconductor processes on silicon wafers. They possess a different storage mechanism and will transform energy storage and pulsed-power applications. Ultracapacitors are reaching widespread adoption and they are now available to support electronics through transportation. New advancements in materials will enable high-energy density devices with exceptional power capabilities.

Chapter 1: Concept Overview

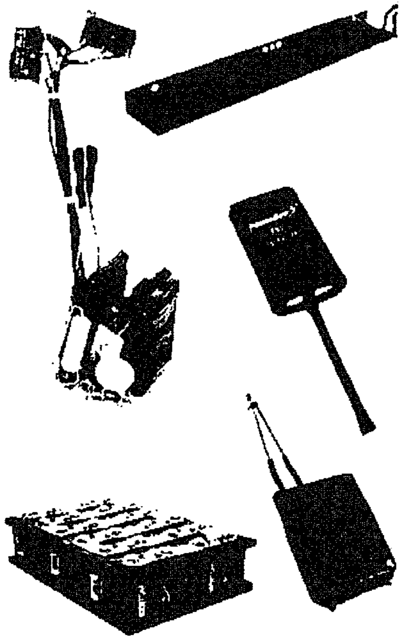


Figure 1. Ultracaps in Various Configurations.[1]

Ultracapacitors, also known as supercapacitors, hybrid capacitors, electrochemical capacitors, electrochemical double-layer capacitors, or ultracaps, are energy-storage platforms that offer energy storage capable of extremely rapid charge and discharge rates. Ultracapacitors also have the ability to be cycled hundreds of thousands of times. The phenomenal charge and discharge capabilities make them ideal for supporting volatile memory and computing applications, energy efficiency/capture processes, and high-power applications. Ultracaps store their charge in the electrical double layer between the electrode and the electrolyte. Charge storage is a physical mechanism rather than a chemical phase change, so these are theoretically capable of cycling an infinite number of times.[2] One of the disadvantages of ultracaps can be a high self-discharge rate.[3] The charge and discharge voltage output for an ultracap is a sloping linear curve, which allows for straightforward and accurate state-of-charge monitoring.[4] The real advantage of an ultracapacitor is the ability to deliver or accept bursts of power in a short time.

Ultracaps were introduced in 1966 and found initial use 12 years later as backup power devices for volatile memory and clocks. Over the last 30 years, numerous advances have been made that have led to many uses of ultracaps, from transportation to portable electronics and more. Ultracaps are becoming more affordable as activated carbon electrodes and manufacturing improvements have driven costs down. Several companies now make ultracapacitors to fill a broad spectrum of applications. Figure 1 shows a number of ultracaps with various capacities to fill a range of functions. Transportation, microelectronics, and aerospace markets are some of the many areas where ultracaps have become enablers. Advanced materials and improved cell designs will lead to improvements in both power density and energy density. The improved performance is expected to make ultracaps important components for efficient power leveling and high-power receiving and delivery. The unique signature of ultracapacitors must be understood for aerospace and military applications.

As an electrochemical capacitor, ultracapacitors store energy within the electric double layer formed at the interface between the electrode and electrolyte. In a conventional capacitor, the energy is stored by moving charge carriers from one plate to another, and the charge separation creates a potential. Voltage differentials in a conventional capacitor are dependent upon the dielectric material separating the plates. In the ultracap, the electrical double layer is the separation of charge in a vanishingly thin gap between two plates. Figure 2 depicts the components and basic design of the ultracap, showing the electrochemical double layer responsible for the characteristic performance.[5] The basic principles of operation have not changed with improved technologies, only the materials and cell design.

The two electrode plates are traditionally the same material, which is usually a carbonaceous material, such as activated carbon. Each layer is capable of storing a low voltage, and multiple layers serve to increase the potential. Individual cells are placed in series to create a higher voltage, in much the same manner as a battery. Recent advances in ultracapacitors have moved toward employing dissimilar electrodes, which create a higher potential; since the electrodes are now different, these are sometimes referred to as "pseudo" or hybrid capacitors. The pseudocapacitor uses a battery-like electrode to replace one of the carbon electrodes, yielding a high-energy-storage electrode and a highly capacitive electrode within the same system.

The capacitance of an ultracapacitor can be determined by the Helmholtz equation (equation 1), which describes the relationship between the electrolyte and the electrode:

$$C = \varepsilon A/d \qquad (1)$$

Here, ε is the dielectric constant of the electrolyte, A is the available surface area, and d represents the distance between the center of the double layer and the electrode surface. Increasing the double-layer capacitance in an ultracap is generally accomplished by either manipulating the electrode (carbon) surface area or the electrolyte. Energy density (equation 2) is the product of the capacitance and the square of the voltage:

$$E = \tfrac{1}{2} CV^2 \qquad (2)$$

Strategies for increasing the stored energy target improvements to both the electrodes and the electrolyte. Changing from an aqueous electrolyte to an organic electrolyte with a higher dielectric constant will increase the voltage from approximately 1 volt to more than 2.5 volts. Increasing the surface area of the electrode is another approach to increasing storage capability. There is a tradeoff between porosity and surface area that must be considered when constructing an electrode with an extremely high surface area. An activated carbon approaching a measured surface area of 3,000 m^2/g may have less than half that as accessible or useable area.[6] Increasing the pore size sacrifices surface area but provides more accessible material. By providing more interfacial area between the electrode and the electrolyte, a better electrochemical double layer can be produced, yielding a better ultracapacitor.

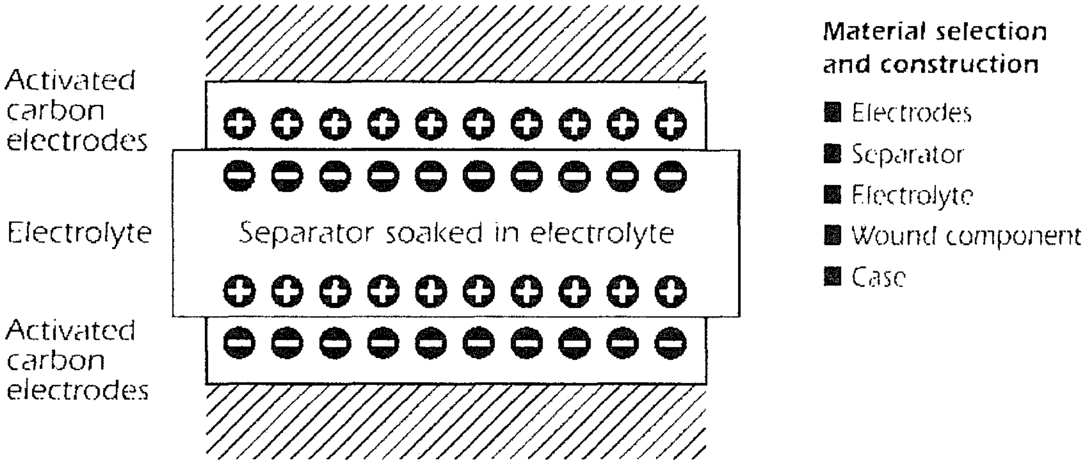


Figure 2. Operation of an Ultracapacitor. A simple ultracapacitor utilizes two similar electrodes (typically carbon) with a separator and electrolyte to create the electrochemical double layer that governs operation.[7]

BATTERIES AND ULTRACAPS

For an ultracapacitor, energy is stored within the electrical double layer, which is a physical storage mechanism. Contrast this with batteries, where charge and discharge take place through a chemical (Faradaic) reaction. Since charge is stored physically, there is no direct degradation mechanism that limits cycle life. Side reactions do occur, which prevents infinite cycle life, but ultracaps can often be cycled tens of millions of times.[8] Batteries store their energy through chemical reaction; consequently, cycle life is much shorter and heavily dependent on the depth of discharge. In contrast, there are no limitations to the discharge depth with an ultracapacitor. Table 1 addresses some of the general characteristics of batteries and ultracapacitors, which can help to determine the preferred system for a specified application. The values are based upon 2008 data, so some numbers are outdated, but the relative values remain consistent. There are now hybrid devices that blur the boundaries further by introducing a battery-like electrode to replace one of the two identical electrodes in a traditional ultracapacitor.

Table 1: Contrasting Properties of Batteries and Ultracapacitors[9]

Characteristic State of the Art	Lithium Ion Battery	Ultracapacitor
Charge time	~3-5 minutes	~1 second
Discharge time	~3-5 minutes	~1 second
Cycle life	<5,000 @ 1C rate	>500,000
Specific Energy (Wh/kg)	100-200	5
Specific power (kW/kg)	0.5 -1	5-10
Cycle efficiency (%)	<50% to >90%	<75 to >95%
Cost/Wh	$1-2/Wh	$10-20/Wh
Cost/kW	$75-150/kW	$25-50/kW

The voltage curve for an ultracapacitor is proportional to the depth of discharge, whereas batteries deliver a relatively constant voltage over a long discharge period. The sloping voltage curve of an ultracap can be advantageous for state-of-charge determinations. However, this is also responsible for the decreased energy density available in an ultracapacitor. For applications requiring energy to be delivered over a longer time scale or delivered at a constant voltage, the relatively flat voltage curve found in most batteries would be the preferred option. In instances where power is to be delivered or received quickly, or where many cycles are required, an ultracap is ideal.

To better understand the differences between batteries and ultracaps, it helps to think of batteries as storing watt-hours of energy and ultracaps as storing watts of power. A Ragone plot illustrates the distinctions by plotting power versus energy in a logarithmic scale. As can be seen in Figure 3, ultracaps make an excellent option where high power density is required. The times shown are rough estimates for a full charge or discharge, which are estimates to help understand the relationship between energy density and power density. Batteries have made significant improvements to power delivery recently, but batteries remain the high-energy-density solution. Ultracapacitors are often thought of as a stop-gap between conventional capacitors and batteries. Recent developments of hybrid capacitors have led to considerable progress toward higher energy density. However, there is a tradeoff between high energy density and high-power devices, and the distinctions between the two require consideration of application requirements when choosing the energy storage platform for a system. The differences between ultracaps and batteries do not make the two mutually exclusive. There are applications where either a battery or an ultracap is the preferred energy storage platform. Quite often, these two can be used together in systems to perform complementary roles.

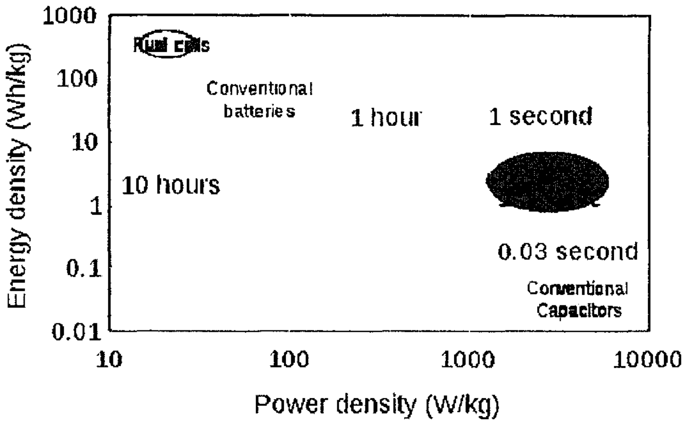


Figure 3. Ragone Plot. The graph illustrates the areas where ultracaps and batteries dominate in the power density versus energy density relationship.

HISTORY

The concept of storing electrical energy in the electric double layer that is formed at the interface between an electrolyte and a solid has been known since the late 1800s. In 1966, Standard Oil Company of Ohio (SOHIO) invented the device in the format now commonly used, which forms the basis for hundreds of patents and thousands of journal articles. Figure 4 shows a drawing from the electrochemical double-layer device invented by SOHIO. NEC introduced the SuperCapacitor^{TM} in 1978 under license from SOHIO.

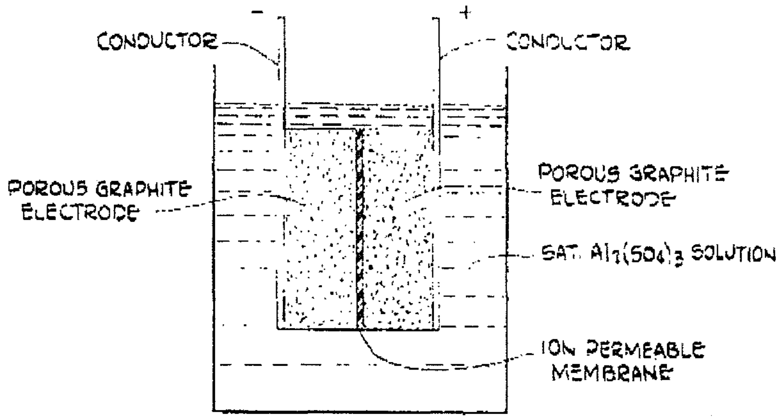


Figure 4. Electrolytic Capacitor as Designed and Patented by SOHIO.

From this point on, ultracaps have rapidly evolved through several generations of designs. In the 1980s, Matsushita Electric Company developed a method of manufacturing ultracapacitors with improved electrodes. Initially, they were used as backup power devices for volatile clock chips and complementary metal-oxide-semiconductor (CMOS) computer memories. As the technology became more understood, more and more applications were developed for ultracaps. Many other applications have emerged over the past 30 years, including wireless communication, power quality, and improved energy efficiency through regenerative energy capture processes, as found in hybrid electric vehicles.[10]

Initial ultracaps used aqueous electrolytes made with $Al_2(SO_4)_3$ (aluminum sulfate), H_2SO_4 (sulfuric acid), or KOH (potassium hydroxide) . While these electrolytes have excellent ionic conductivity, the operating voltage is limited to 1.2 volts using carbon electrodes. Organic electrolytes have lower ionic conductivity, but the higher dielectric constant increases the nominal cell voltage up to as high as 3 volts. Carbon has been used as a high-surface-area electrode material since the inception of the electrochemical capacitor. It is still the material of choice for many ultracapacitors; one of the primary reasons is the low cost of carbon materials. However, there are many types of carbon that are available for use as an electrode material. In addition to carbonaceous electrodes, metal oxides and conductive polymers are finding increasing use in ultracap design. Advancements in the understanding of the electric double-layer and ultracapacitor behavior have led to better materials utilization and, consequently, improved devices.

Early electrochemical capacitors were rated at a few volts and had capacitance values measured from less than one farad up to several farads. Today cells range in size from small devices with exceptional pulse-power performance in the millifarad range up to devices rated at several kilofarads. There are even some specialized ultracapacitor cells now in production that have ratings of more than 100 kF. The technology is experiencing increasingly broader use, replacing batteries in some cases and in others complementing their performance. Ultracap technology has grown into an industry with sales of several hundred million dollars per year that is poised for rapid growth in the near term due to expansion of power quality needs and the emerging energy management/conservation applications.[11]

Advancements in ultracapacitors have led to numerous devices from an array of manufacturers. Table 2 compares the various products on the market, showing voltage, capacity, power density, and additional energy-storage characteristics. Ultracaps have moved away from aqueous electrolytes and are typically organic electrolytes due to the increased voltage performance. Electrodes vary from carbon/carbon systems to hybrid systems using metal oxides or conductive polymers paired with a carbon electrode. Packaging and sizes of ultracapacitors covers a large range as these are now used from cellular communications and small electronics to power delivery and management for seaport cranes. Ultracapacitor technology development is focusing on delivering better energy density, and this is being approached by improved carbon electrodes, better electrolytes, and alternative electrodes that provide pseudocapacitive behavior, including battery-like electrodes.[12]

Table 2: Manufacturers of Ultracapacitors[13]

Device	V rated	C (F)	R (mOhm)	RC (sec)	Wh/kg (1)	W/kg (95%) (2)	W/kg Match. Imped.	Wgt. (kg)	Vol. lit.
Maxwell*	2.7	2,885	.375	1.08	4.2	994	8,836	.55	.414
Maxwell	2.7	605	.90	.55	2.35	1,139	9,597	.20	.211
Apowercap**	2.7	55	4	.22	5.5	5,695	50,625	.009	---
Apowercap**	2.7	450	1.4	.58	5.89	2,574	24,595	.057	.045
Ness	2.7	1,800	.55	1.00	3.6	975	8,674	.38	.277
Ness	2.7	3,640	.30	1.10	4.2	928	8,010	.65	.514
Ness (cyl.)	2.7	3,160	.4	1.26	4.4	982	8,728	.522	.38
Asahi Glass (pc)	2.7	1,375	2.5	3.4	4.9	390	3,471	.210 (est.)	.151
Panasonic (pc)	2.5	1,200	1.0	1.2	2.3	514	4,596	.34	.245
EPCOS	2.7	3,400	.45	1.5	4.3	760	6,750	.60	.48
LS Cable	2.8	3,200	.25	.80	3.7	1,400	12,400	.63	.47
BatScap	2.7	2,680	.20	.54	4.2	2,050	18,225	.50	.572
Power Sys. (AC, pc) **	2.7	1,350	1.5	2.0	4.9	650	5,785	.21	.151
Power Sys. (GC, pc) **	3.3 3.3	1,800 1,500	3.0 1.7	5.4 2.5	8.0 6.0	486 776	4,320 6,903	.21 .23	.15 .15
Fuji Heavy Industry- hybrid (AC/GC) **	3.8	1,800	1.5	2.6	9.2	1,025	10,375	.232	.143
JSR Micro (AC/GC)**	3.8	1,000 2,000	4 1.9	4 3.8	11.2 12.1	900 1,038	7,987 9,223	.113 .206	.073 .132

(1) Energy density at 400 W/kg constant power, Vrated - 1/2 Vrated
(2) Power based on $P=9/16*(1-EF)*V^2/R$, EF=efficiency of discharge
* Except where noted, all the devices use acetonitrile as the electrolyte (pc = propylene carbonate)
AC = Activated Carbon; GC = Graphitic Carbon
** Laminated pouches; all other devices are packaged in metal containers

Chapter 2: Materials Technology

The standard electrochemical capacitor is made of two electrodes, an electrolyte, and a separator, packaged in either a metal container or a laminated pouch. Ultracapacitors are often packaged in a fashion similar to a typical battery configuration. The separator is an ultrathin material that allows ion transport but is electrically insulating. There are several polymer separators on the market that have the desired porosity needed to create fast ion transport. The electrodes are traditionally the same material in an ultracapacitor—this is in stark contrast to a battery. Electrodes are typically carbon; this is advantageous in making a cost-effective energy/power-storage device. Activated carbon has a very high surface area, vital to storing energy in the electrical double layer between the electrode and the electrolyte. This thin double layer is responsible for the impressive high-power-storage capabilities of the ultracapacitor. The electrolyte's resistivity and dielectric constant play a vital role in behavior of the double layer; consequently, the choice of electrolyte impacts performance.

The earliest electrochemical capacitors were introduced 30+ years ago; they were symmetric designs (two identical electrodes) in aqueous electrolyte. While these electrolytes have excellent ionic conductivity, the operating cell voltage was limited to ~1.2 V/cell and these had a nominal cell rating of ~0.9 volts. In the second generation of electrochemical capacitors, the use of organic electrolyte led to an increase of the rated cell voltage from about 0.9 V/cell to 2.3-2.7 V/cell. Today, ultracapacitors using an organic electrolyte are the most popular.[14]

ELECTROLYTES

Initial ultracaps used aqueous electrolytes, saturated with $Al_2(SO_4)_3$, or 30% concentrations of H_2SO_4 or KOH. While these electrolytes have excellent ionic conductivity, the operating voltage is limited to 1.2 volts using carbon electrodes. Improvements to ultracapacitor performance were made by transitioning from aqueous electrolytes to an organic medium. Organic electrolytes have lower ionic conductivity, but the higher breakdown potential increases the nominal cell voltage. An increase in cell voltage up to as high as 3 volts has been realized by use of an organic electrolyte. These electrolytes are typically an ammonium salt dissolved in an organic solvent, such as propylene carbonate or acetonitrile. Table 3 highlights the comparison between the various electrolytes used in ultracapacitors. Ionic liquids are beginning to become more common in ultracapacitors, as they allow for an increase in cell voltage to as high as 4 volts. These ionic liquids have a higher resistivity, especially at lower temperatures. The tradeoff in resistivity for voltage may be beneficial for some high-power applications.

Table 3: Properties of Various Electrolytes Used in Ultracapacitors[15]

Electrolyte	Density (gm/cm3)	Resistivity (Ohm-cm)	Cell Voltage
KOH	1.29	1.9	1.0
Sulfuric acid	1.2	1.35	1.0
Propylene carbonate	1.2	52	2.5-3.0
Acetonitrile	0.78	18	2.5-3.0
Ionic liquid	1.3-1.5	125 (25°C)	4.0
		28 (100°C)	3.25

ELECTRODES

Carbon has been the optimal electrode material for ultracapacitors since their commercial introduction over 30 years ago. Pseudocapacitor systems use a combination of a carbon electrode and a battery-like electrode, such as a conductive polymer or a metal oxide. The high surface area of carbon makes it an extremely attractive option for ultracap electrodes. Carbon chemistry is quite well known, and high surface area and low cost ensures carbon's continued use for the near future. While carbon has been used in electrochemical systems for many years, there are many nuances that make its properties and performance vary significantly amongst the many types of carbon. The use of a carbon electrode makes ultracaps affordable for use in many systems. Activated carbon is readily available, can be made from many source materials, and is inexpensive. Materials science activities for electrodes are focused on improving the carbon electrodes and introducing alternative materials to create an asymmetric electrode.

Types of carbon can include activated carbon, carbon cloth, aerogels, porous carbon, carbon nanotubes, and graphene. The properties of carbon can change dramatically based upon processing, having a major impact to the porosity and active surface area. Activated carbon has an extremely high surface area, is inexpensive, and is produced at a global scale for use in a number of applications. For these reasons, activated carbon is the traditional carbon of choice for ultracapacitor applications. Recent advances in carbon materials development have led to a number of options for ultracapacitor electrodes. Table 4 demonstrates a number of electrode materials in use today and the corresponding performance of these ultracaps.

Table 4: Properties of Various Materials Used in Electrochemical Capacitor Electrode Materials[16]

Material	Density (g/cm^3)	Electrolyte	F/g	F/cm^3
Activated Carbon	0.7	KOH	160	112
		Organic	100	70
Carbon Cloth	0.35	KOH	200	70
		Organic	100	35
Aerogel Carbon	0.6	KOH	75	
		Organic	125	84
Porous Carbon from SiC	0.7	KOH	175	122
		Organic	100	70
Porous Carbon from TiC	0.5	KOH	220	110
		Organic	120	60
Anhydrous RuO_2	2.7	Sulfuric Acid	150	405
Hydrous RuO_2	2.0	Sulfuric Acid	650	1,300
Doped Conductive Polymer	0.7	Organic	450	315

Activated carbons are synthesized by a heat treatment of carbon-rich organic precursors in a controlled atmosphere. This carbonization process can be performed from natural sources, such as fruit shells, wood, pitch, or coke. Activated carbons can also be produced from synthetic precursors, such as select polymers. The heat treatment process uses a controlled partial oxidation of the precursor combined with a high-temperature processing. The high-temperature processing can be done in an inert atmosphere, an oxidizing environment, or with a chemical modification. The activated carbons contain a distributed porous network throughout, as shown in Figure 5.[17] These materials can have an extremely high surface area, upward of 3,000 m^2/g, but process conditions to create activated carbons have little control over pore size distribution, resulting in incomplete utilization of the surface area. Carbon cloth electrodes use processing conditions similar to those used to create activated carbons. The advantage with a fabric composed of activated carbon is these materials are directly used as active electrodes, requiring no binder or additional processing. However, these tend to be expensive to produce, which has thus far limited their use to specialized applications.

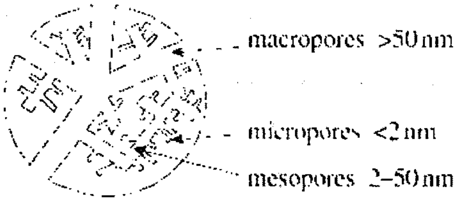


Figure 5. Activated Carbon Porosity. These can be produced with a distribution of pore sizes ranging from less than 2 nm to greater than 50 nm.

Continued improvements to the carbon electrodes are expected to provide additional performance enhancement to ultracaps. Current research is leading toward carbon materials with higher specific capacitance (F/g). Improved materials, such as carbon nanotubes and tailored porous carbons show promise as the next generation of carbon materials. Graphene is another advanced carbon material that shows promise to providing increased capacitance. One of the key design issues revolves around improved understanding of the relationship between the carbon pore size and the electrolyte ion. The nanostructured materials allow fine tuning of the porous structure to increase capacitance.

Carbon nanotubes (CNTs) are commonly produced as powders where they can be cast as a distributed network to form an electrode, and they can be used as an additive to increase conductivity. Additionally, CNTs can be grown as a "forest," where the CNTs are grown perpendicular to a substrate. These forests can be used as is or can be modified or coated to change specific structural or electronic properties. CNTs are grown by a number of methods, but most methods used currently are a derivative of a chemical vapor deposition (CVD) process. The specific properties of the nanotubes are extremely tailorable. CNT length, diameter, the number of tubes, and the electronic properties can all be tailored by growth conditions. The catalysts used to grow CNTs can affect tube properties, as well as CNT temperature and precursor variables. Carbon nanotubes are finding utility in both battery and ultracapacitor applications, where they are used for conductivity enhancement and energy storage. Their capacitive behavior suggests they may have a fundamentally different storage mechanism than traditional carbon. Storage potential includes CNT outer walls, inner diameter, and interwall spaces of some CNT types. Carbon nanotubes have been a rich area of study for many applications, which has translated to a broad understanding of synthesis techniques to produce CNTs with tailorable properties.

Graphene can be thought of as a sheet of graphite, either a single layer or a few layers thick. The two-dimensional nature of graphene leads to extremely high electron transport across the surface, interesting magnetic properties, high strength, and a large accessible surface area.[18] Graphene is generally made by exfoliation/separation of graphite or grown by CVD processes. Derivations from both of these methods can produce single-layer graphene or few-layer graphene. These methods include, but are not limited to, CVD methods, epitaxial growth, solvothermal synthesis, micromechanical exfoliation, and colloidal synthesis.[19] Graphene has generated an enormous amount of attention due to its potential for transforming electronics. A number of approaches to graphene synthesis are being used that consider purity, scalability, and cost.

Carbide-derived carbons are a unique class of porous carbons with extremely fine control over pore size.[20] These porous carbons are derived by chlorination of metal carbides at very high temperatures. At temperatures of 500–1000°C, metals and metalloids are removed as chlorides, leaving behind a finely tunable nanoporous carbon. These porous carbons have a pore-size distribution that is tunable within 0.05 nm. The extremely accurate tunability has allowed these systems to serve as a model for the relationship of pore size and capacitance, thereby allowing for design of materials to be tailored for maximum capacitance within a specific system. The local maximum in capacitance is dependent on the ion solvation sphere, which is a product of the electrolyte ion, solvent, and interaction with the pores of the electrode. These findings will lead to new electrode materials and designs.

Activated carbon and other porous carbon derivatives are commonly used for symmetric ultracapacitors. Metal oxides such as ruthenium oxide and conductive polymers replace one of the electrodes to create an asymmetric system. Asymmetric electrodes greatly increase the storage capacity of ultracapacitors. These are a different class of capacitor, as they store their charge both in the electrical double layer and using a surface redox (faradaic) reaction (in the same manner as a battery). While these undergo electron transfer reactions, they behave in a capacitive fashion. Often termed pseudocapacitor, this class of materials includes a variety of metal oxides and conductive polymers. The capacitance of an asymmetric electrode is twice that of a symmetric design. The electron transfer electrode essentially has a fixed potential, whereas the potential of the carbon electrode changes with state of charge. Additional storage capacity arises from the higher working voltage, due to the different rest potentials of the different electrodes.

Asymmetric electrodes are becoming increasingly common due to the increased energy-storage capability. As energy is proportional to the voltage squared, the higher operating voltage has profound effects on the capacity. Ruthenium oxide (RuO_2) has been shown to give capacitance of as high as 1300 F/cm^3. By comparison, carbonaceous materials in an aqueous electrolyte have a capacitance of 110-125 F/cm^3. There are many additional metal oxides being investigated for insertion into the ultracapacitor system. Many of these have their roots in lithium ion battery cathode materials. As ultracaps gain wider acceptance, market size is increasing rapidly and is expected to grow at an increasing pace. Investigations are being conducted into alternative metal oxide systems to ensure that cost, supply, and performance can be met on a global scale. Manganese oxide (MnO_2) and nickel metal oxides/hydroxides are leading alternative candidates for asymmetric ultracaps. Using a pseudocapacitive design will most likely not be able to deliver the cycle life of a symmetric ultracap, but it may be possible to achieve tens of thousands of cycles out of a battery-like electrode. Better capacitance and higher operating voltage of the asymmetric electrode design allow ultracapacitors to begin approaching batteries in terms of energy density.

Additional ultracapacitor improvements will come from materials and cell design. Cell design factors include optimization and assembly techniques. Thinner electrodes and current collectors will be one of the primary paths for better performance. Electrolytes that provide cell voltages of at least 3 volts will be standard. Improvements such as these will likely lead to improvements in commercially available ultracaps from 4 Wh/kg to 5-6 Wh/kg.[21]

Chapter 3: Applications

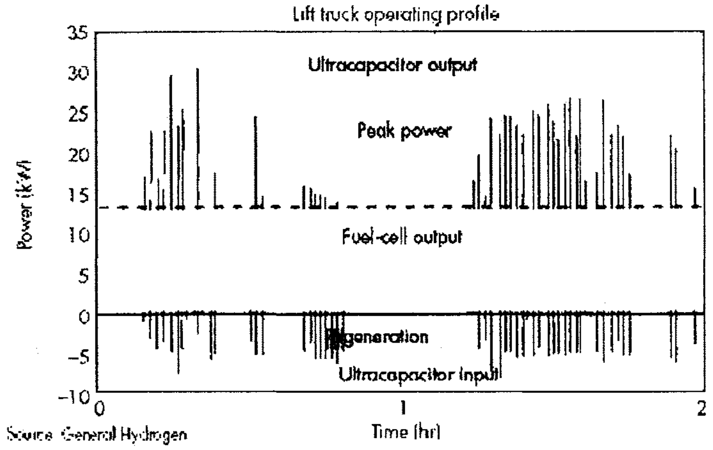
ELECTRONICS AND TELECOMMUNICATIONS

The most straightforward application of an ultracapacitor is to stabilize dc voltages, which is where they have found widespread use. Areas where a dip in voltage may occur and negatively impact performance is another natural fit for ultracaps. Initially, they were used as backup power for clock chips and CMOS memory; now, they find utility in power smoothing, flash photography, and digital cameras. Flash for mobile phone cameras is an ever-increasing market. Nearly one billion phones equipped with cameras were sold in 2009. Ultracaps enable flash photography integrated with mobile communication. Today's market is driving toward electronics devices with multiple functions to eliminate the need for multiple specialized electronics that each performs one task. Integrating components into one electronic device requires the use of ultracapacitors to help stabilize the short power spikes from the individual components. Ultracaps also serve to reduce thermal loading from power dissipation.

Ultracaps have found extensive application in wireless communication, where they are used in wireless data cards for GSM, GPRS, and WiMAX data transmission. The peak current required during data transmission can exceed what is available under USB or PC-card standards, and the excess current is delivered with an ultracapacitor. Automated meter reading is another application where ultracaps have become an integral component, as the power required to send and receive the meter information is handled by an ultracapacitor. The mobile telecomm industry is currently using these in a number of ways; it is likely that additional uses for ultracaps will spring up along with needs to balance power requirements for increasingly complex and multifunctional devices contained within smaller areas.

INDUSTRIAL

Industrial applications are becoming much more ubiquitous as ultracaps are being used as a platform to deliver a large amount of power quickly. These are becoming increasingly important in cranes, forklifts, elevators, and power tools. As an example, power is stored by an ultracapacitor in hybrid forklifts every time a loading fork descends. The stored power is then delivered to the forklift when heavy lifting is required. Figure 6 shows the power requirements for a hybrid forklift. The peak power pulses are areas where using an ultracap to deliver or to receive the power greatly improves the operational efficiency. The blue shaded area represents the power distribution handled by a fuel cell, and the tan regions above and below the blue area represents the output from and the input to the ultracapacitor, respectively.[22] In cranes and elevators, a similar application is used. Peak power is supplied for lift operations by the ultracap. During descent of the elevator or lowering of the loaded crane, generated power can be used to recharge the ultracapacitor. Power tools are becoming increasingly disconnected from an outlet. Many of these cordless power tools require significant amounts of peak power, which many batteries cannot adequately supply. The ultracapacitor used in conjunction with a high energy battery supplies the pulse power required during heavy use.



Source: General Hydrogen

Figure 6. Ultracapacitor Use in a Forklift. Ultracaps provide energy storage upon descent of a load and deliver peak power to lift heavy loads in fuel cell powered forklifts.[23]

Grid storage management is gaining more visibility as energy conservation and efficiency are becoming increasingly important. Many utility power sources generate a relatively continuous supply of electricity. The generated power is matched to expected use statistics. Daytime use and nighttime rest periods can cause power shortages or generate unused power if not managed efficiently. This is especially true during the hot summer months or heat waves, where air conditioning loads can tax a system. Ultracapacitors can store excess power generated in the night, which can then be delivered when insufficient power is available to match the daytime needs. Distributed power sources such as wind and solar require a higher level of operational efficiency with a fluctuating power supply. Wind farms experience power fluctuations due to wind shear or lack thereof. These spikes in power generation may be wasted on a system ill-equipped to handle the burst of power delivered. During periods where wind may be lacking, ultracapacitors can be used to help create a more stabilized power supply.

TRANSPORTATION

Earliest uses of ultracapacitors were in motor startup for tanks and submarines. Early adoption by the military led to cost reductions, which was a critical enabler for incorporation into diesel trucks and railroad locomotives. Ultracapacitors are finding use in transportation in engine startup, braking systems, acceleration, and waste-energy harvesting. Ultracaps have been placed in rail cars to generate power for acceleration and recapture it during braking. In some cases, they are placed alongside the tracks, and the power management is hosted by the rail stations.

The ability to absorb and discharge energy rapidly makes ultracapacitors far better than batteries for regenerative braking schemes. Most of these applications have been in public transportation. Regenerative braking can recuperate as much as 38% of the propulsion energy when used in an ultracap/battery hybrid configuration. Electric hybrid public buses were some of the first adopters of ultracapacitors for automotive transportation. These buses also use ultracaps for acceleration, which enables a much faster acceleration.

AEROSPACE

Ultracapacitors are suitable for applications requiring large bursts of power for relatively short periods of time, with the ability to be recharged rapidly. Ultracapacitors are finding ubiquitous use in electronics and transportation, and there are a number of applications in aerospace ranging from backup power to high pulse-power delivery. The electronics systems in military vehicles require failsafe operation; ultracaps can be designed to provide a continuous power source in the event of a power interruption. Fire-control systems are another example where continuous power is required, including higher power capability. Airbags require a backup power source to ensure they are deployed as required with or without a powered system. Small portable communications systems have ultracaps for backup power and to retain memory. Memory retention is critical in many systems; for example, the bridge power used during a transfer from ground to onboard power in aircraft systems can be supplied by an ultracap. Ultracaps are excellent for stabilizing the power that is either delivered or received. For example, communication systems may require additional power during transmission, which can be offset by using an ultracap to supplement the system. Bus voltages may need peak current stabilization.

The high-power capabilities of ultracaps make them advantageous for several systems. The fast discharge is ideal for delivering the significantly higher power required for starting cold engines. Active suspension systems in vehicles require bursts of power that are delivered in response to the terrain; an ultracap can store the necessary power, deliver as necessary, and recharge quickly. GPS-guided missiles and projectiles may use ultracapacitors to provide the power required for communication and navigation. High-power discharge for naval systems has been identified as an area where ultracaps are especially useful, often used in hybrid systems in tandem with high-energy batteries. Extremely high power delivery makes ultracapacitors a potential vehicle for delivering the power required for directed-energy weapons. As pseudocapacitive systems reach higher energy densities, along with improvements to the materials and cell composition, ultracapacitors will have capabilities of delivering large amounts of power in a very short time, contained within an increasingly smaller footprint.

Signatures and Vulnerabilities

As mentioned above, ultracapacitors could be important in the development of ultrawideband energy weapons. Previously, this market has been dominated by bulk acoustic semiconductor switch (BASS) devices, but by stringing several capacitors together in parallel, a more formidable discharge can be created. Because ultracapacitors have very high discharge rates, they will emit a distinctive broadband RF signature when discharged. A modest wideband receiver may be able to detect this discharge; its proximity will depend upon the construction of the target device. Furthermore, the architecture of such a device may yield a unique signature that, with the proper equipment, can be identified and certainly warrants further study. When employed in a particular electronic device, this signature may be altered by its immediate environment, and this may further give an indication of both the type of use and device employed. When searching for ultracaps in the field that are not in use, the large electrostatic potentials may provide a clue.

Stimulated Discharge

Depending on the application and the implementation and construction of ultracaps in sensitive or destructive applications, vulnerabilities likely exist and warrant study in areas of research such as circuit vulnerability analysis, reversible manufacturing and construction techniques used in fabrication, stimulation of nondestructive and controlled discharge evaluations, and laboratory stimulated discharge experiments.

Chapter 4: Recent Developments

There have been several recent advances in ultracapacitors focused on increasing energy density by using different active materials[24] and designs,[25] activated carbons,[26] polymers,[27] and metal oxides.[28] Conducting polymers have good performance,[29] but lack microfabrication protocols. Oxide-based thin-film ultracaps have shown high performance, approaching the theoretical limit for capacitance (~1,000 F/g for MnO_2).[30] However, the poor electrical conductivity and high impedances associated with surface intercalation redox reactions of these oxides have limited practical film thicknesses to a few microns. Carbon nanotubes have been added to the films to increase the electrical conductivity, but the complexity of manufacturing limits practical applications of such composite electrodes. In this section we will discuss advances in application of CNT and advanced carbons to ultracapacitor materials, the application of thin-film manufacturing processes, and a revolutionary new super capacitor using a giant magneto capacitive effect.

CNTS AND ADVANCED CARBONS

Carbon electrodes constitute both electrodes in a symmetric ultracapacitor and one of the electrodes in an asymmetric, or pseudocapacitive, design. Improvements to the carbon electrode rely upon increasing the specific capacitance (in Farads per gram). These improvements come by tailoring the surface area and porosity to achieve the best balance that maximizes the interaction with the electrolyte. There is a linear relationship to the surface area and the capacitance up to a point where capacitance plateaus with activated carbons. By controlling the porosity and surface area, it is possible to increase the capacitance beyond this plateau. Carbon nanotubes could provide performance increases with aligned CNT forests of tailored sizes. The characteristics of an ultracapacitor are highly dependent on the nanostructure of the carbon used for the thin-film electrodes. Advanced carbons will provide better control over the pore size and distribution, leading to an expected 50- to 100-percent improvement over the carbons in use today.

Carbon nanotubes can be produced with a wide variety of properties. Depending on synthesis parameters, nanotubes can be single walled or multiwalled, with varying numbers of tubes. CNT diameters can be tailored from a few nanometers to tens of nanometers, with lengths up to hundreds of microns. CNTs can be grown in random orientations or as aligned forests. CNTs have a fully accessible surface area and very high electrical conductivity. Methods for incorporating CNTs into electrodes for ultracaps include using CNTs as an additive for conductivity enhancement, creating dense mats of randomly oriented tubes, and creating electrodes from vertically aligned forests of tubes. Initial results of CNT-enabled ultracaps tended to show much lower capacitance than expected, which has been attributed to the hydrophobic nature of the CNT walls. Surface functionalization is a common approach to mitigating the hydrophobicity issues and thus enabling higher capacitance. Another benefit of the functionalization is the ability to introduce and control pseudocapacitance.

Most efforts in CNT ultracaps are directed toward vertically aligned forests. It is possible to controllably grow a dense, aligned forest that is perpendicular to the current collector. The size and density of the tubes and the number of walls can be controlled with catalyst design and reaction parameters. Manipulation of the CNT forest leads to increased capacitance by fine-tuning the distance between tubes. Additionally, fine-tuning the inner diameter may provide further enhancements. Figure 7 shows a vertically aligned CNT forest produced at Lockheed Martin's Advanced Technology Center (LMATC). Lockheed Martin has worked with a number of catalysts and surfaces to grow tailored CNT forests for a variety of applications. Select locations throughout Lockheed Martin have been developing CNT-based technologies, utilizing vertically aligned CNTs, CNTs dispersed onto surfaces, and CNTs dispersed into other media. LMATC possesses expertise in CNT growth processes and characterization and has capabilities for both materials development and ultracap testing. Lockheed Martin's NEARLab facility produces CNT-coated glass fibers, which may provide a cost-effective power storage solution that has structural elements built in. Ultracaps assembled from CNT forests appear extremely promising for use in microelectronics.

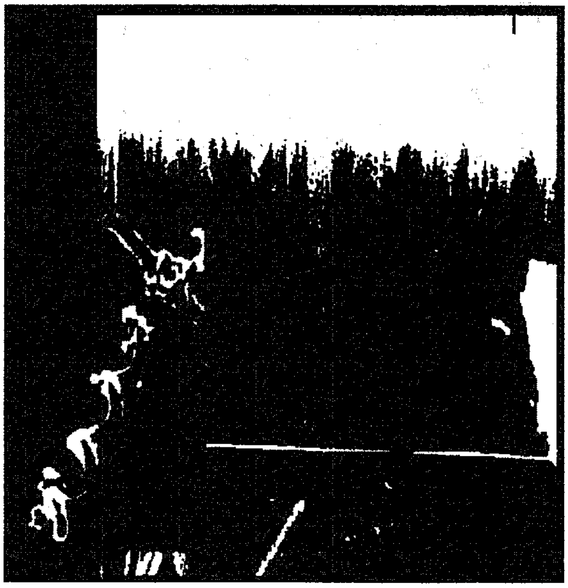


Figure 7. CNT Forest. CNT forests grown in Lockheed Martin's laboratories can be tailored for specific sizes, lengths, and densities.

Graphene is a relatively new discovery amongst carbonaceous materials. There are a number of types of graphene that can be characterized by the number of layers of graphene, the functionalization, or the oxidation status. Most graphene for ultracapacitor applications is going to be few-layer graphene and large-area flakes. The fewer the layers, the higher the active surface area will be. Single layer is ideal, but manufacturing considerations make single layer difficult, even at the laboratory scale. Functionalization will be directed toward improving capacitance or modifications to enable battery-like performance.

Theoretical values of graphene indicate it could become an important material for the next generation of ultracapacitors. Graphene may be used as the sole electrode material, or it could be used as a conductive additive that also provides capacitance. The surface area is calculated to be as high as 2,600 m^2/g, the thermal conductivity is 5,000 W/m·K, and the charge carrier mobility is 200,000 $cm^2/V{\cdot}s$. High surface area values and great conductivity are ideal properties for creating an electrode with very high capacitance and extremely favorable rate capabilities. Reported capacitances range from 135 to 205 F/g in aqueous electrolytes.[31, 32] Figure 8 shows a transmission electron microscope image of graphene flakes used for ultracapacitor electrodes. These measurements come from few-layer graphene, rather than single layer, which suggest there is room for improvement on these values. Optimization of graphene synthesis to produce finer control is an area receiving increased attention in research and development activities in universities, national labs, and industrial research facilities. Lockheed Martin is actively engaged in research investigating graphene and applications where graphene could be a critical differentiator. There are a number of companies that supply graphene made from various methods, as well as emerging startups geared toward producing graphene-based ultracapacitors or materials designed for ultracaps.

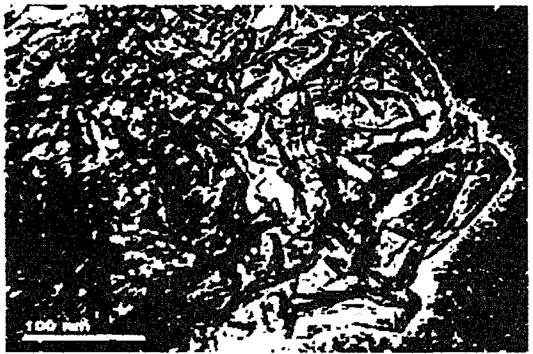


Figure 8. Transmission Electron Microscope Image of Graphene. This could be an excellent ultracapacitor electrode material with its high surface area and excellent conductivity. [33]

Manipulation of the porosity of high surface area carbons leads to the largest difference in specific capacitance. Understanding the relationship between the electrolyte ion size and the carbon pore size is critical to improving performance. There are a number of strategies being investigated for fine control over the pore-size distribution to increase the specific capacitance. The most common methods used currently are template methods and carbide-derived carbons. Template methods create a controlled mesoporous structure with a fairly narrow range. These structures have pores that range from 2 to 10 nanometers and are maximized to pore sizes roughly twice that of the solvated ions. The template process involves filling the pores of an inorganic template host with a carbon precursor (such as an alumina template). The template is removed after carbonization by acid treatment. The pore size is then dictated by the template as the pores are the remaining void space once occupied by the template. Similar methods have shown that smaller pores, including those less than two nanometers, may provide high specific capacitance. The realization that smaller pores contribute to charge storage in an electric double layer has led to the need to develop a better understanding of the charge storage mechanism.

Carbide-derived carbons have a unique pore-size distribution that is tunable with sub-angstrom accuracy. These have served as models to study the charge storage behavior and ion adsorption in pore sizes ranging from 0.6 nm to 1.1 nm.[34] The normalized capacitance decreases with decreasing pore size until a critical value is reached. Figure 9 shows the relationship between average pore size and the normalized specific capacitance. Pore sizes smaller than one nanometer significantly contribute to the charge storage despite the fact that the solvated ion size is larger than the pore diameter. The capacitance increase is explained by a distorted ion shell model. The ion solvation shell is perturbed such that it is capable of a closer approach of the ion and the carbon surface. The discoveries at Drexel University that utilize the fine control to create tailored porous carbon structures can maximize specific capacitance for a given ultracapacitor system.

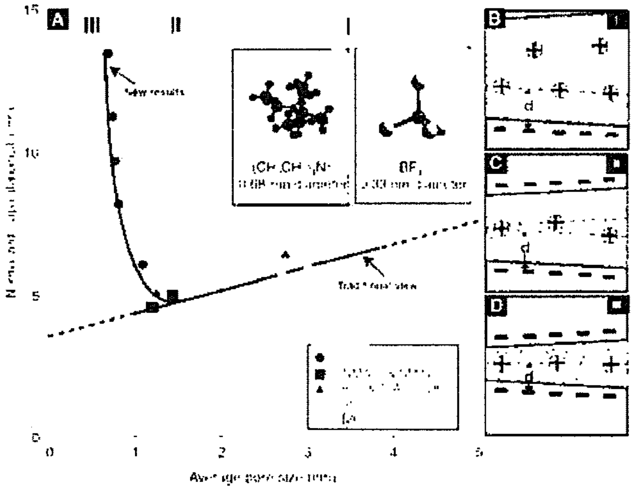


Figure 9. Relationship Between Average Pore Size and Normalized Specific Capacitance. As the average pore size decreases below 1 nm, the specific capacitance increases due to distorted electrolyte ion solvation.

THIN FILMS

CNT films have been used in 2D thin-film ultracapacitors having respectable gravimetric and volumetric capacitance. Activated carbon powders have a better performance in terms of energy per unit area,[35] but they need to be processed into films before use, and this limits their choice for microdevice fabrication, which allows mass production of capacitors on semiconductor wafers. Carbide-derived carbon (CDC) is a class of carbon materials produced by selectively etching metals from metal carbides using chlorine at elevated temperatures in a process similar to current dry-etching techniques used in MEMS and microchip fabrication. CDC has been shown to have excellent performance as the active material in traditionally processed ultracaps[36] since it can have its microstructure precisely tuned by tailoring the synthesis conditions for a particular electrolyte.[37]

For microfabricated supercapacitors, CDC is attractive for several reasons. The precursor carbides are conductive and can be deposited in uniform thin and thick films by well-known chemical and physical vapor deposition (CVD and PVD) techniques.[38] In addition, the chlorination process can be performed at temperatures at least as low as 200°C,[39] and the resulting coatings are well-adhered with an atomically perfect interface,[40] which minimizes device impedance. This technology can be used to produce the microfabricated ultracaps on the same chip as the integrated circuits, which they are powering (shown in Figure 10).[41] Chlorine-containing plasma etching of materials in semiconductor manufacturing is a well-established technique and is similar to the chlorination procedure in CDC manufacturing. Continuous porous carbon films cannot be produced by conventional CVD, PVD, or other techniques, and the high-temperature activation needed to produce the microstructures necessary for ultracapacitor performance in CVD carbons would destroy the devices they were intended to power.

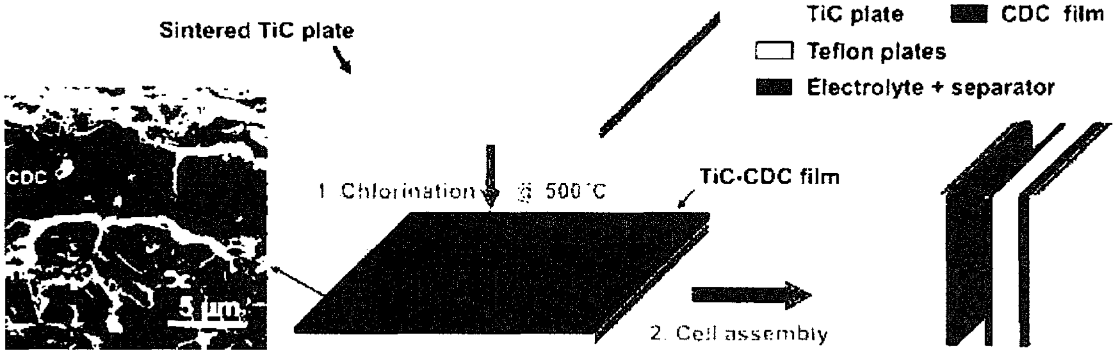


Figure 10. CDC Synthesis and Electrochemical Test Cell Preparation Schematic.[42]

Electrochemical measurements of CDC films were carried out in a three-electrode configuration with a large, overcapacitive activated carbon counter-electrode in both 1M $TEABF_4$ and 1M H_2SO_4, as well as two-electrode cells with symmetric bulk CDC film electrodes. Volumetric capacitance was calculated for each of the different film thicknesses (shown in Figure 11). For both $TEABF_4$ and H_2SO_4, the volumetric capacitance decreases with increasing coating thickness. This is especially pronounced in the organic electrolyte, where there is a huge increase in volumetric capacitance as the film thickness decreases from 200 to ~2 mm.

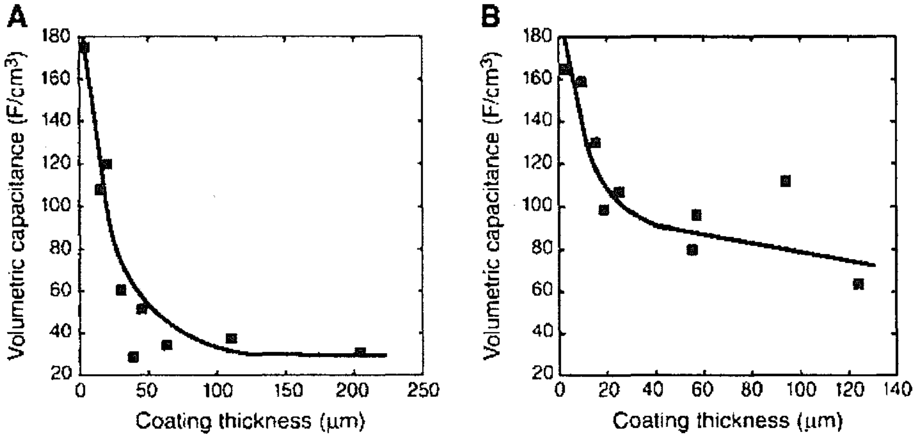


Figure 11. Volumetric Capacitance of the Films in (A) $TEABF_4$ and (B) H_2SO_4.[43]

MAGNETIC CAPACITORS

Giant magneto capacitance (GMC) is a quantum mechanical effect observed in thin-film structures composed of alternating ferromagnetic and nonmagnetic layers.[44, 45] Such materials have been reported to have increased permittivity by 10^9.[46] This material behavior normally occurs at temperatures well below 273K and has only recently been reported in the literature above this temperature.[47] However, since 2007, Northern Lights Semiconductor Corp. (NLSC) has been developing a magnetic capacitor (MCap) that utilizes a material which exhibits the GMC above 300K.

Structured like the basic flat-plate capacitor, an MCap nanocell features a proprietary dielectric layer sandwiched between two magnetized layers. Each magnetic material layer is made of multiple nanometer-thick thin-film layers. Millions of MCap nanocells are created and linked using a semiconductor thin-film process, producing the MCap cell on a wafer (Figure 12).

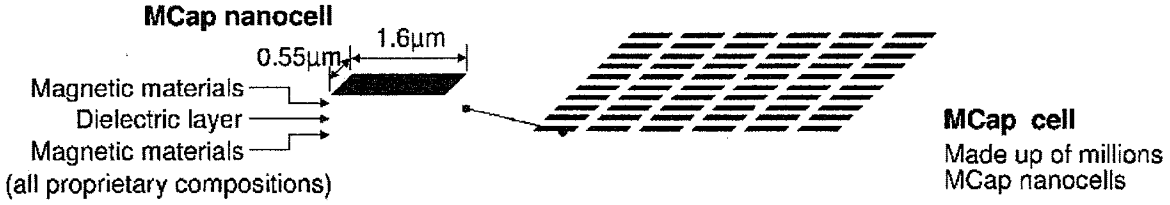


Figure 12. MCap Structure. MCap nanocell and MCap cell are fabricated using traditional semiconductor fabrication processes.

MCap cells are then packaged into larger MCap modules. The capacitance of the device is given by the equation , $C = \varepsilon_0 k A/d$, where A is the area of the plate, d is the separation between plates, ε_0 the permittivity of free space, and *k* is the dielectric constant (or relative permittivity) of the material. The MCap increases capacitance by increasing the dielectric constant *k* through the GMC effect ($\mathbf{f}_{GMC}$) given by the relationship, $k' = k*\mathbf{f}_{GMC}$. GMC acts like a charge trap that brings electrons closer, thus increasing electron densities at the plates. Based on quantum theory, GMC brings about a capacitance which, to date, has been measured to be 10^9 times larger than that observed in electrostatic capacitors. As shown earlier in equation (2), energy is proportional to the capacitance and the voltage squared. Moreover, capacitor leakage and self-discharge are essentially eliminated as electrons are "trapped" in the magnetic field.

Due to the above effects, the available energy for a large range of storage devices, like smart cards and other products, can be increased substantially by simply packaging them in series-parallel connected modules to meet the energy and voltage requirements. Coupled with Lockheed Martin's extensive nanomaterials and device physics experience, it is likely that NLSC will be able to use its MRAM development expertise to accomplish this.

Experimental Results

Over the last year, NLSC has had MCap structures and nanocells tested by independent parties with results shown in Figure 13. These unbiased tests demonstrate the validity of the high-capacitance claims. Figure 14 quantifies the progress in improved performance throughout the development of the device. The number of devices that demonstrate the GMC behavior has increased substantially in 2009, which is reportedly due to improved materials development rather than an increased production load. The performances of the nanocells as well as the variability are plotted, which shows that potential improvement in the materials could lead to an increased GMC factor. There is promising evidence that improvements may allow a higher level of performance, which could match lithium ion batteries at ambient temperature and perhaps exceed them at low and high temperatures.

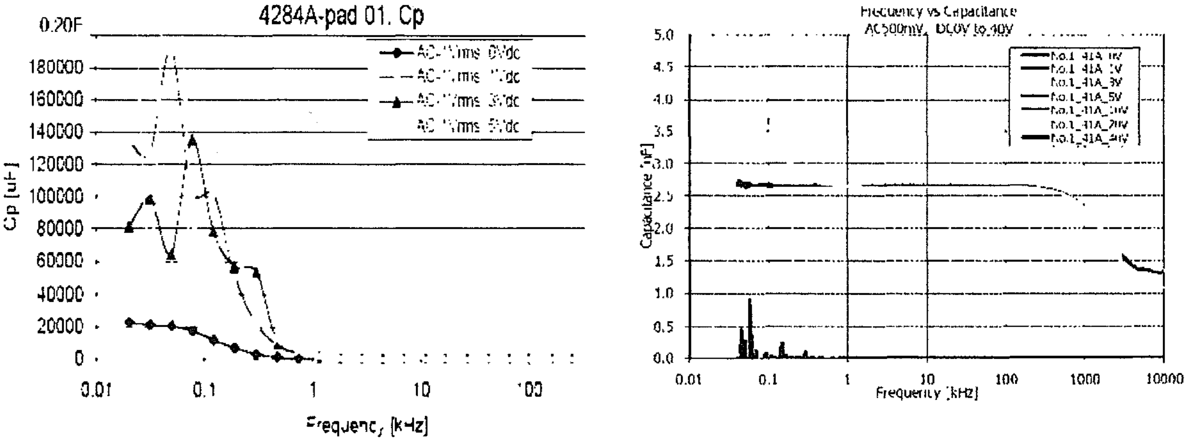


Figure 13. Preliminary MCap Test Results. These graphs demonstrate NLSC capabilities: MCap microstructure tested at different VDC (by Taiyo Yuden) (left) and single nanocell tests (right).

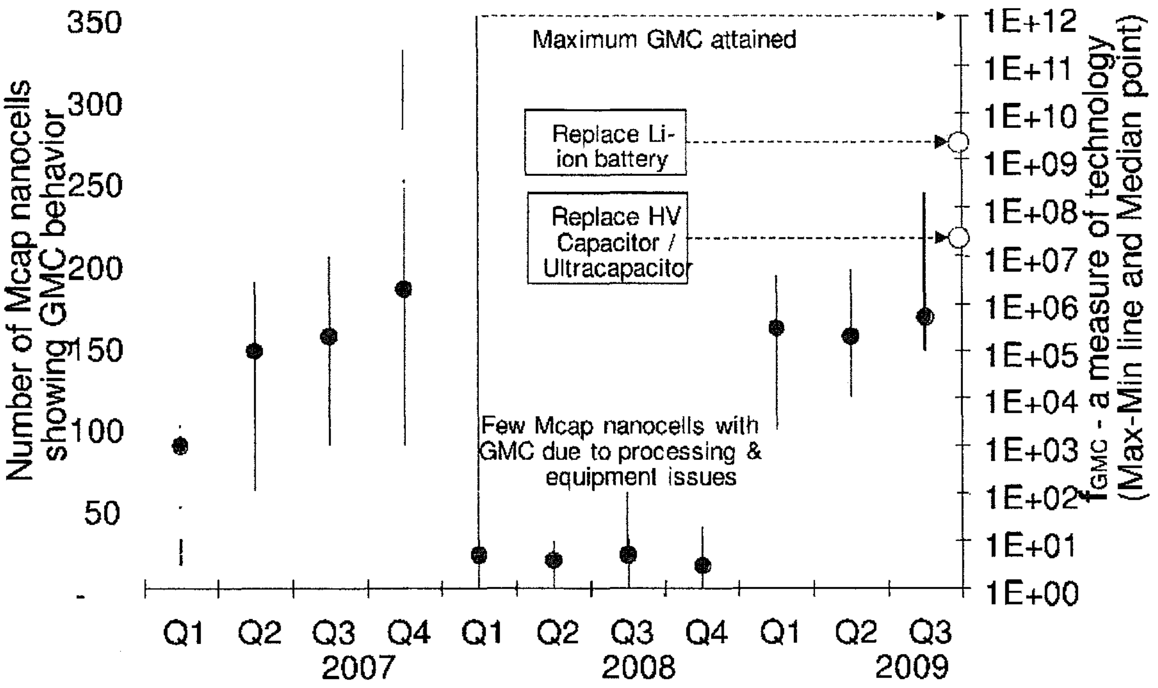


Figure 14. Summary Chart of MCap Results to Date. Right Axis: High-Low value lines in red, Median value in black dot. Left Axis: number of nanocells exhibiting GMC phenomenon in blue bar.

Figure 15 shows an estimate that has been made by NLSC of the potential specific energies and projected manufacturing costs of the MCap for comparison to current energy storage devices.

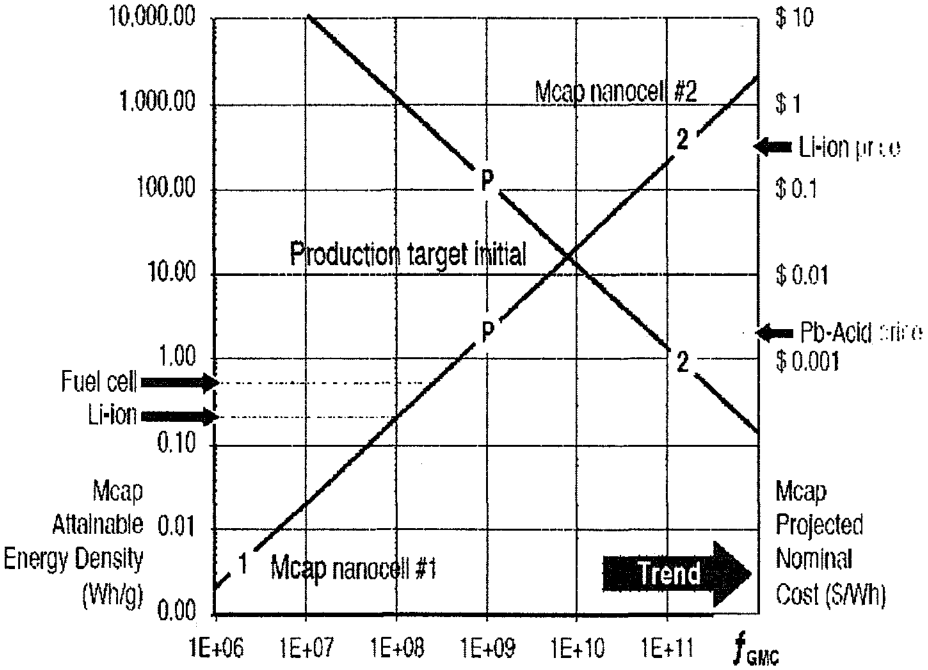


Figure 15. Specific Energy and Estimated Costs vs. f_{GMC}

The mass production target of MCaps on a wafer of $\mathbf{f}_{GMC}$ of ~10^9 would enable the achievement of exceeding the specific energy of lithium ion batteries at a significantly reduced cost. MCaps at these production targets would disrupt both the lithium ion battery and the ultracapacitor market.

Chapter 5: Future Developments

There have been significant advancements in ultracapacitor technology in the last few years. Increased understanding of the physical mechanism behind this technology, combined with advancements in materials science, particularly on the nanoscale, has led to a rapid increase in capability. Improvements to ultracaps in the next 10 years (2010-20) will focus on electrodes, better electrolytes, packaging, and alternative designs. Electrode improvements will most likely include migration away from activated carbon, for both electrodes. Asymmetric electrodes will eliminate carbon on one side, and new carbon materials will provide better performance at a competitive price. Electrolytes will likely move toward additional organic materials and ultracaps with high temperature performance requirements likely will use ionic liquids.

In the near term, a transition to the asymmetric design is expected. Continued improvements to the electrodes and cell design will provide better capacitance. Many of the short-term improvements will likely be directed toward manufacturing capacity. Ultracapacitors are becoming more common, and as improvements to performance and cost make them more accessible to multiple applications, this trend will continue. Over the next few years, it is expected that the market for ultracaps will increase dramatically. Trends in materials for ultracaps will continue forward with improvements and utilization of activated carbons, thinner current collectors, and improved cell design and packaging. Research being done at universities and national labs will continue, but these will not become common materials for ultracapacitors in the next few years. However, as the demand for ultracapacitors increases, specialty materials will begin to see utility for some applications, driving down manufacturing costs, which in turn will enable their use in more systems. Significant use will be made in integrating into power converters to reduce size, mass, and cost. Both thin-film and MCap devices will become prevalent. If MCaps achieve lithium ion specific energy their adoption will be rapid and revolutionary as has occurred with $LiFePO_4$ (lithium-iron-phosphate) batteries for both transportation and extremely high pulsed-power systems such as lasers.

Within the next 10 years, ultracaps will begin to see the incorporation of advanced carbon materials and electrodes designed with features on the nanometer scale. Carbon nanotubes, graphene, and porous carbons all have extremely high potential to unseat activated carbon as the electrode of choice. The replacement of carbon systems being used today (including activated carbon, aerogels, and carbon cloths) will occur as cost reductions take place in the manufacturing of nanostructured carbonaceous materials. The tradeoff between surface area and pore size can be exploited at the nanoscale. Optimization of these parameters will likely yield fairly significant improvements to the capacitance and result in higher power and better energy density.

The mid-range (2020-30) development of ultracapacitors will most likely be the full incorporation of advanced carbons and hybrid systems. It is hard to anticipate which technology has the most to offer, as there are unique benefits and hurdles for each. Hybrid systems will be common, utilizing a battery-like electrode combined with one of the advanced carbon electrodes. The pseudocapacitive electrode options will become diversified, with manufacturers using unique materials to differentiate their product. An alternative electrode to the ruthenium oxide (RuO_2) used today will be used for both performance and economical reasons. Supply issues will drive electrode materials toward those with larger availability.

In the 2020-2030 timeframe, ultracapacitor cell designs will be different. Simple plate designs, coin cells, and laminated pouches will still be used for some applications. However, advanced designs and form-factors will be used to fit specialized applications. Ultracapacitors will be designed for incorporation into chip architectures. Several options will exist for micro- and nano-electronics. Electrolyte options will most likely be different from those used today. New electrolyte solvents and better salts will be discovered that produce higher voltage cells while maintaining good ionic conductivity. Ionic liquids and complex solvents that withstand higher voltages are likely candidates. Three dimensional architectures may begin to be introduced, which will greatly improve both energy density and power density. Manufacturing techniques will enable small- and medium-format three-dimensional electrodes, where the electrical double layer is stored perpendicular to the current collector. The manufacture and assembly of large-format ultracapacitors with extremely high power capabilities will be enabled by three-dimensional architectures of nano-engineered carbons and current collectors.

Beyond 2030 it is difficult to project the future developments of ultracapacitors since materials science is experiencing a nanomaterials revolution. It can be expected, however, that nearly all microelectronic circuitry will incorporate thin-film ultracaps or MCaps, and laptop computers will become the size of an iPhone with mostly voice-activated functions. As depicted in Figure 16, advancements will occur on a much faster timescale than what has happened over the last 50 years.

In the energy storage area, particularly for PHEV and EV batteries, the major impact for ultracapacitors may allow not only reduced mass and size but also order-of-magnitude reduction in costs.

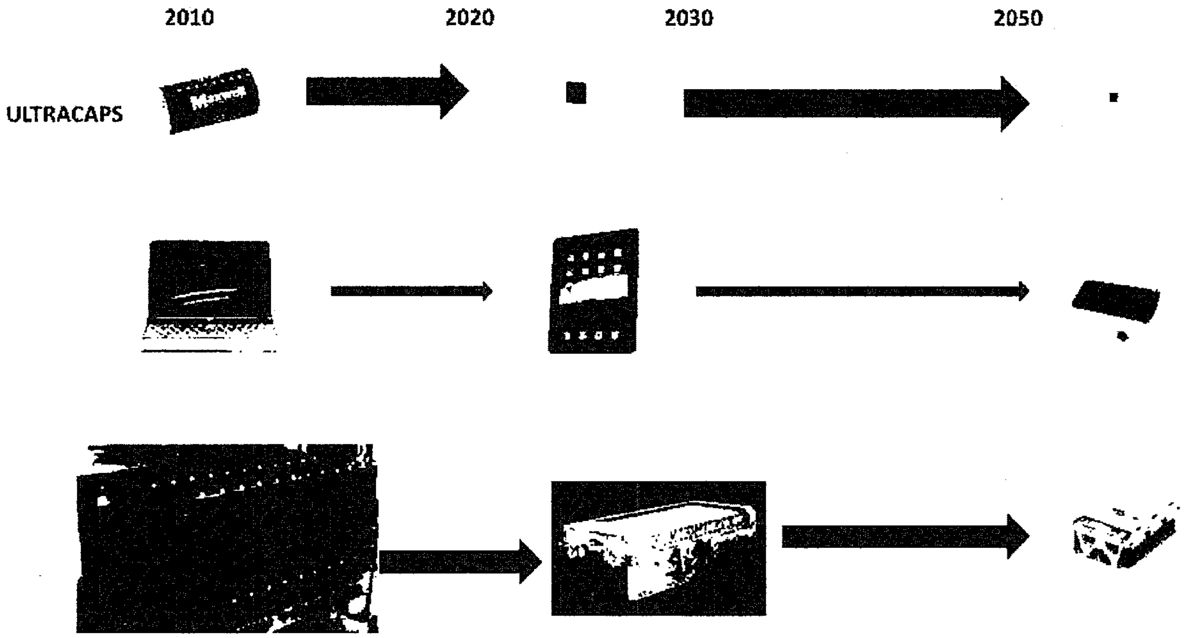


Figure 16. Evolution of Ultracapacitors

Chapter 6: Conclusions

Ultracapacitors are becoming increasingly important in applications ranging from portable electronics to cargo transport cranes. Their introduction in electronic circuits for conversion and storage assistance will become the next major milestone. The virtually unlimited cycle life combined with high power capabilities has made them an integral component to many energy-management schemes. Early adoption of ultracaps by the military was an important differentiator for vehicle performance and a technology driver. Improvements to activated carbons and manufacturing techniques have brought costs down. The ultracapacitor is relatively young and is expanding rapidly as ultracaps are reaching a more widespread audience. Increased adoption has led to recognition of the benefits, and the attention has allowed researchers to develop a better understanding of the power-storage mechanisms.

New materials and cell designs will produce increased capacitance and higher voltages, which will in turn give ultracapacitors better energy density. Advanced carbons show great promise to generate a carbon electrode with much higher capacitance than the activated carbons in use today. These include porous carbons, carbon nanotubes, and graphene. Capacitance increases by the carbon electrode alone could double the energy density. Additional advantages in conductivity and the ability to functionalize these materials will generate improvements in power density as well as energy density. Hybrid systems utilizing a battery-like electrode are beginning to gain acceptance. These pseudocapacitive systems maintain the high power density of a symmetric ultracap and also have substantially higher energy density. While these systems sacrifice some cycle-life capability, it appears as though they will survive tens of thousands of cycles.

Ultracapacitors are a solution for generating or absorbing high pulse power. They also are excellent devices for backup power and stabilization of fluctuating power requirements. Increased power densities and energy densities will open up new applications for ultracaps, replacing fuel and batteries in some cases, supplementing them in others. Power management and generation for military systems will see increasing uses for ultracaps. Their unique capabilities will enable future designs. Their specific performance capabilities must be optimally utilized and we must have a keen understanding and awareness of the unique spectral signatures these devices generate when storing high power and in charge or discharge modes. Development of these advanced ultracaps must be performed, understood, and adopted by the U.S. government and those who are developing the systems to be used by the government.

Chapter 7: Endnotes

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